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# MONTHLY TECHNICAL REPORT FOR AUGUST AND SEPTEMBER 1944

on

# FLUOROCARBON RESEARCH AT HOOKER ELECTROCHEMICAL COMPANY

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Submitted By:

R L Murray


October 20, 1944

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Technical Report on
Fluorocarbon Research at Hooker Electrochemical Company
August and September 1944

## ABSTRACT

1. Work on P-46 is now being held in abeyance until instructions to proceed are issued by the U.S.E.D.

2. It may be possible to improve Step-2 yields in the P-46 process by altering slightly the distillation procedure used in the removal of the Step-2 product from the reactor.

3. No improvement in the preparation of the Step-2 product was detected when the order of adding the reactants together was reversed.

4. U.S.E.D. requested Hooker to examine Dr Miller's M.F.L. process in the laboratory and pilot plant and then authorized the production of 100 gallons to be completed on or about October 1st.

5. By elevating the reaction temperature 50°C the reaction period for the polymerization of the monomer P-539 was shortened considerably.

6. The conversion of cobalt difluoride to cobalt trifluoride can be accomplished in a simple reactor without the application of external heat or agitation. Approval of U.S.E.D. was granted to use fresh cobalt difluoride each time instead of complicating the production of the 100 gallons of M.F.L. by attempting the re-use and regeneration of spent cobalt difluoride.

7. To insure the production of M.F.L. with good stability characteristics, a 2 stage treatment of the polymer with FM33 was worked out and employed.

8. The preparation of M.F.L. was carried out in the original P-45 plant, the maximum of existing U.S.E.D. equipment being utilized plus some additional equipment which was installed.

9. The distillation of the crude M.F.L. polymer and the finished M.F.L. were carried out by the Distillation Products Inc., at their plant at Rochester, New York. D.P.I. did an excellent job and cooperated with Hooker and U.S.E.D. in a most excellent manner. (We wish to thank also, in passing, Dr Miller for his moral support)

10. 97 gallons of finished M.F.L. (all approved as to quality by Kellex) were produced at an over-all yield based on P-539 of 18.25%. It is possible that this yield will be boosted somewhat by a further treatment of the residues from the crude polymer distillation which is now under investigation.

11. The development of the M.F.L. process through pilot plant stage, the construction of the necessary plant and the production of 97 gallons (goal 100 gallons) in such a short space of time was made possible by splendid cooperation on the part of du Pont (in supplying the necessary monomer), U.S.E.D., D.P.I., and the various departments involved in the Hooker Company.

Technical Report on
Fluorocarbon Research at Hooker Electrochemical Company
August and September 1944

## I. P-46 PROCESS -STEP II- TREATMENT OF POLYCHLOROHEPTANE WITH HF IN THE PRESENCE OF $SbCl_5$

### A. The Preparation of 5,000 Pounds of P-46

Further work on the completion of the 5,000 pound P-46 order is being held in abeyance pending instructions from U.S.E.D. to proceed with its fulfillment. At present, P-46 facilities are being used for the manufacture of M.F.L. Thus, difficulty would be encountered in completing the P-46 order, in the very near future, unless additional equipment is made available to replace that required by M.F.L. production, which is continuing.

### B. Laboratory Studies on P-46

#### 1. Attempts to Improve the Conversion of Polychloroheptane to P-46

To avoid the recycling of more than 60% of the Step-2 material through the still in which the isolation of P-46 is effected, a series of experiments were performed wherein only the more highly fluorinated haloheptanes were removed from the reactor during hydrofluorination. The high boiling, less completely fluorinated, chloroheptane was allowed to remain in the reactor for recycling with the next charge. The procedure employed for these runs was essentially the same as that used in the usual runs whereby the ratio of organic to $SbCl_5$ was 1 to 1, with the exception that after the chlorine content of the organic in the reactor dropped to about 45% only that portion of the Step-2 material which distilled over when the body temperature of the reactor reached 135°C was collected for rectification to P-46. The organic remaining in the reactor along with the spent salts was used in making up the next charge which consisted of adding fresh polychloroheptane equivalent to the fluorochloroheptane removed (about 20% of the original charge) and from 10 to 20% $SbCl_5$ based on the quantity of fresh haloheptane being added to the reactor.

The average chlorine content of the Step-2 material thus obtained was 24-25% and its content of product boiling below 138°C ranged from 40-50%. It is of interest to note (Table I - July report, and Table I - this report) that the amount of material distilled from the reactor, after the initial run is completed, corresponds to an average yield of 92% based on the conversion of the newly added chloroheptane to $C_7H_xCl_{2.5}F_{9.5}$. Due to mechanical difficulties, neither of the two series started was continued beyond the 4th run, hence it is not known how much longer the higher yields could have been maintained before it becomes necessary to refill the reactor with an entirely new batch of raw materials.

Technical Report on
Fluorocarbon Research at Hooker Electrochemical Company
August and September 1944

2. The Addition of $SbCl_5$ and Chloroheptane to Liquid HF

The effect of low temperature in the conversion of chloroheptane to P-46 was investigated by reversing the order in which the reactants were allowed to commingle. A single phase, one to one by weight, mixture of chloroheptane and $SbCl_5$ was gradually added to liquid HF at -12 to +12°C. Upon completing the addition of the organic and antimony salts, the mixture was kept at the low temperature for one hour before elevating it to 70°C where it was held for another hour prior to removal by distillation as in the usual runs. A Step-2 product containing 29% chlorine in 82.5% yields was obtained. This does not constitute an improvement in the process. No attempt was made to evaluate the quality of the P-46 isolated from this run.

## II. THE PREPARATION OF M.F.L.

### A. General

On August 11th, Major G W Russel and Captain W M Hearon told Hooker of their urgent need for 1 to 100 gallons of M.F.L. The product was to be made available to the U.S.E.D. by the first of October. Having indicated the status of the preliminary investigations pertaining to the synthesis of M.F.L., only a portion of which was checked at Hooker, it was agreed that the preparation of the 100 gallons would be started as soon as possible using the best data available regardless of source. Approximately three weeks were spent by the Engineering and Research Departments in arranging available U.S.E.D. equipment in the original P-45 plant for the production of M.F.L. Since necessary high vacuum distillation equipment was not available at Hooker nor could it be installed in time to meet the October 1st production schedule, arrangements were made to have the distillation carried out at Distillation Products Inc., in Rochester, New York.

Production of M.F.L. was started August 16 and a total of 97 gallons was produced by October 4. Samples of the finished product were sent to the Kellex Laboratories for approval prior to shipment.

As a result of the pilot plant work carried out in June and July, a few changes which helped to speed up production were incorporated in Dr Miller's M.F.L. process. Essentially the process consists of 4 steps or chemical reactions which may be illustrated as follows.

Step I. Preparation of the Monomer (Product 539)

$$\underset{\text{Freon 113}}{CF_2Cl - CFCl_2} + Zn \xrightarrow{EtOH} \underset{\text{Monomer (P-539)}}{CF_2 = CFCl} + ZnCl_2$$

Technical Report on
Fluorocarbon Research at Hooker Electrochemical Company
August and September 1944

Step II. Polymerization of the Monomer.

$$CF_2 = CFCl \text{ (P-539)} + \text{Benzoyl Peroxide} \xrightarrow{CHCl_3} (CF_2 - CFCl)x \text{ Crude Polymer}$$

Step III. The preparation of Cobalt Trifluoride.

$$2\,CoF_2 + F_2 \longrightarrow 2\,CoF_3$$

Step IV. Stabilization of the Crude M.F.L.

$$(CF_2 - CFCl)_y + CoF_3 \longrightarrow (CF_2 - CFCl)_y + CoF_2 + HF + Cl_2$$

Crude polymer fraction — M.F.L.

B. Experimental Work

Step I. Preparation of the Monomer (P-539)

Since most of the monomer which was to be used in the production of the 100 gallons of M.F.L. was to be furnished by du Pont all experimental work on this phase of the synthesis was discontinued.

Step II. Polymerization of the Monomer

To shorten the time cycle in the polymerization of P-539, a series of pilot plant runs were made in which the catalyzed chloroform solution of the monomer was heated to 150°C and held there for 10-15 minutes instead of 100°C for 2 hours as recommended by Dr Miller. The reaction under these conditions proceeded in a straight forward manner, yielding a crude polymer in quantity and character identical to that obtained by the somewhat longer reaction period. Samples of the crude polymer were examined and approved by Dr Miller. Thus, for plant operation the shorter reaction period was employed for M.F.L. production.

Step III. The Preparation of Cobalt Trifluoride (FM 33)

To accumulate data pertinent to the construction of a reactor for the conversion of cobalt difluoride to cobalt trifluoride, a series of tests were conducted in which fluorine was passed over the difluoride set in the trays of the HF absorber attached to the large fluorine cell. This work revealed that the transformation of fresh difluoride to the trifluoride could be readily accomplished in a simple reactor without the application of external heat or agitation. Samples

examined showed a uniform conversion to a product assaying 90% of theory as cobalt trifluoride. In order not to further complicate a very full program, U.S.E.D. agreed that we should not attempt to regenerate the spent cobalt salt and fresh cobalt difluoride was therefore used exclusively for conversion to the trifluoride.

Step IV. Stabilization of The Crude M.F.L.

A small reactor for the treatment of crude M.F.L. with $CoF_3$ was constructed and used in a series of experiments to furnish data for plant operation and a sample of the finished product for appraisal. The need for efficient and powerful agitation became evident when a 1 H.P. motor equipped with an anchor type agitator installed in a 1/2 gallon vessel seized due to the nature of the charge. To avoid this difficulty in plant operation and to insure the production of a product with excellent stability characteristics, a two stage FM-33 treatment was recommended as indicated later in this report. Based on the charge of organic used for the FM-33 treatment, the yields of the final product varied considerably (i.e.60-80%) and were somewhat lower than had been anticipated. The yield fluctuations were probably caused by inadequate fractionation during the removal of the pay cut from the crude polymer. A five pint sample (C.P. 334-44) of the product prepared in pilot plant equipment was approved by Kellex as passing all specifications set for M.F.L.

C. The Production of M.F.L.

1. Construction

Building D5 which housed the original P-45 plant was taken over for the production of 100 gallons of M.F.L. Much of the equipment in the building was used in its original location with the exception of the piping which was altered extensively. One autoclave was used for the production of P-539 and another for the polymerization of the monomer. Two of the P-45 neutralizers were used as dilute polymer receivers and three of the 500 gallon glass lined chlorinators as stills for the concentration of the polymer and the recovery of the chloroform. New construction consisted of installing a dry-ice, trichloroethylene cooling and circulating system; three vapor-tight pressure filters; a new 150 gallon glass lined predecomposition vessel and a complete reactor, operating platform, concentration still and other auxiliary equipment for the treatment of the distilled polymer with FM-33.

Since no suitable equipment was available at Hooker for carrying out the high vacuum distillation of either the crude concentrated polymer or the finished M.F.L., arrangements were made to have the work done by Distillation Products Inc., at Rochester, New York. These are difficult distillations to perform and much credit is due D.P.I. for the excellent results which they have obtained on this phase of the problem.

Technical Report on
Fluorocarbon Research at Hooker Electrochemical Company
August and September 1944

2. Plant Operation

Step I. Production of The Monomer (P-539)

The preparation of the monomer was carried out at atmospheric pressure, under conditions described by Dr Miller, in one of the 110 gallon autoclaves. A typical charge consisted of 150 pounds of powdered zinc, 200 pounds of 95% ethanol and 300 pounds of Freon 113 which was added at a rate of 50 pounds per hour while keeping the temperature of the mixture in the clave at 65°C. Since only 1520 pounds of Freon 113 were available, only 5 monomer runs were made. A total of 828 pounds of P-539 was thus produced, the yield being 87.3% (Table II). The monomer produced was immediately polymerized in the next step. No effort was made to recover the ethanol, zinc,or unreacted Freon from the sludge left in the clave.

Step II. Polymerization of The Monomer

The polymerization of the monomer was carried out in another 110 gallon autoclave. In all, 8,628 pounds of the monomer were processed; 7800 supplied by du Pont and 828 pounds prepared at Hooker. A clave charge consisted of 8 pounds of benzoyl peroxide dissolved in 892 pounds of $CHCl_3$ which was dried with soda ash prior to use, and 100 pounds of the monomer Unstabilized monomer prepared at Hooker and recovered P-539 were charged into the autoclave as a liquid. Du Pont's monomer containing a stabilizer was distilled from its container into the solvent in the clave through a $P_2O_5$ scrubber.

To process all of the P-539 (including that recovered) required 104 clave runs yielding 5,723 pounds of the crude concentrated polymer. This accounts for 66.4% of the monomer charged and another 8% appeared as fore-shot from the predecomposition still. ~~Probably the remainder of the monomer is present as low molecular~~ Not so! Probably lost weight polymers being recirculated in the recovered chloroform. The crude polymer was sent down in batches to Rochester in an Army car, for distillation and recovery of crude M.F.L. From 5,723 pounds of the crude polymer concentrate sent to D.P.I., handling 2,900 pounds of crude M.F.L. was obtained for treatment with FM-33. Five hundred and seventeen pounds appeared as volatile material and 2100 pounds as solid residue (Table III).

Step III. The Preparation of Cobalt Trifluoride (FM-33)

Having established the ease with which $CoF_2$ is converted to $CoF_3$, the the existing HF absorber (previously used for removing HF from fluorine cell gas) was used as a production unit for FM-33. To insure continued operation, a spare absorber was constructed and held in reserve in the event FM-33 production lagged or some adverse situation was encountered with the present reactor. A total of

3,104 pounds of the trifluoride was made in the absorber of which 2,956 pounds was consumed in the treatment of 2,900 pounds of crude M.F.L. The amount of cobalt salts needed to stabilize the product could have been reduced considerably if more efficient fractionation had been employed in isolating the pay cut from the crude concentrated polymer. Doubt whether CoF3 consumption will be much lower

Step IV. Stabilization of The Crude M.F.L.

To achieve good stability, the treatment of M.F.L. with FM-33 was carried out in two stages. The first treatment was made with FM-33 amounting to 85% by weight of the organic being stabilized. The addition of the salt was carried out in 3 portions as recommended by Dr Miller. The product was separated from the spent salts by extraction with $CCl_4$ from which it was later recovered by distillation. This material was then retreated in a second reactor using 8-10% FM-33 by weight, and filtered directly from the salts into shipping containers. Spent salts from the second treatment were combined with the batch from the first treatment for extraction with $CCl_4$. The stabilized M.F.L. was also sent to D.P.I. for the final distillation. The distillate was returned as a series of fractions which on proper blending yielded the desired product.

3. Conclusions

A total of 97 gallons of M.F.L. was produced in the plant during the period that it was operated by the Research Department. Based on monomer consumed this amounts to an 18.25% yield which is somewhat lower than the 20% yield anticipated (Table IV). Samples representing drummed lots of the finished product were tested and approved by the Kellex Laboratories.

Unfortunately, time was not available for a thorough study of this synthesis in pilot plant equipment. Undoubtedly, a number of improvements could have been made which would not only simplify operation but also improve the yield of the desired product. For example it may be possible to convert, by a drastic treatment with FM-33, a good portion of the residues from the first distillation to a useable product possessing physical properties similar to M.F.L. No.

III. TRIPS

August 14 - 17 ... W M Ewalt to S.A.M. Laboratories to obtain additional information on M.F.L.

August 23 - 26 ... W M Ewalt and L E Tufts to Kellex Laboratories, Jersey City, N. J. To learn how to test the quality of M.F.L.

Sept. 1 - 3 ... L E Tufts to Kellex Laboratories. To have samples of M.F.L. tested.

Technical Report on
Fluorocarbon Research at Hooker Electrochemical Company
August and September 1944

Sept. 20 - 22 ... W M Ewalt to Kellex Laboratories to eheck on the quality of M.F.L. being produced in the plant.

Sept. 27 - 28 ... W M Ewalt to Kellex Laboratories with additional samples of M.F.L. for testing.

Sept. 28 - 29 ... L E Tufts to Kellex Laboratories to ascertain why samples of M.F.L. were not passing specification tests and to have retreated samples checked.

Oct. 6, 7, 8 ... L E Tufts to Kellex Laboratories to run tests on finished M.F.L. ready for shipment.

A conference was held at Niagara on September 15th, with Dr McBee and three of his men, to discuss Purdue's work on P-46 and its conversion to 715-Cl and 716.

During the months of August, September and the early part of October, numerous trips were made by various members of our Research Department to Distillation Products Inc., at Rochester. These trips covered making arrangements for the distillations, the scheduling of shipments, and a number of technical discussions.

Technical Report on
Fluorocarbon Research at Hooker Electrochemical Company
August and September 1944

TABLE I - LABORATORY DATA ON P-46

| Purpose of Experiment | Pounds Charged | | HF Treatment | | $Cl_2$ Treatment | | Step-2 Product | | Dist. Time Hours | Still Body Temp. °C | % Yield of Step-2 Product | % Yield of P-46 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Organic | $SbCl_5$ | Lbs HF | Temp °C | Lbs $Cl_2$ | Temp °C | R.I. 20°C | % $Cl_2$ | | | | |
| Partial removal of Step-2 Product | 50 | 50 | 24<br>37<br>55 | 27-35<br>40-60<br>58-60 | 10<br>19 | 28-40<br>40-52 | | | | | | |
| Dist. | | | | | | | 1.3680 | 25.5 | 12 | 50-136 | *32.2 | 42 |
| | 16 | 2 | 14<br>21.5 | 40-70<br>52-68 | 10<br>16 | 40-57<br>46-63 | | | | | | |
| Dist. | | | | | | | 1.3650 | 24.5 | 16 | 42-135 | **73.5 | 45 |
| | 11.5 | 1.5 | 14<br>18 | 48-61<br>53-67 | 10<br>19 | 40-56<br>37-52 | | | | | *** | |
| Dist | | | | | | | 1.3650 | 24.5 | 11 | 78-136 | 104 | 49 |
| Addition to Liquid HF | 7 | 7 | 8.25 | -12 to +12 | | | 1.3810 | 29.0 | 13 | 20-180 | 82.5 | |

* Based on the full 50 pound charge of organic
** Based on a 16 pound charge
*** Based on a 11.5 pound charge.

Technical Report on
Fluorocarbon Research at Hooker Electrochemical Company
August and September 1944

TABLE II

The Production of P-539

| Run No. | Alcohol Lbs. | Zinc Lbs. | Freon 113 Lbs. | P-539 Yield Lbs | Yield % of theory |
|---|---|---|---|---|---|
| 1 | 195 | 150 | 273 | 151 | 88.6 |
| 2 | 200 | 150 | 300 | 157 | 84.0 |
| 3 | 200 | 150 | 300 | 148 | 79.0 |
| 4 | 200 | 150 | 300 | 172 | 92.0 |
| 5 | 232 | 174 | 348 | 200 | 92.0 |
| Total | 1027 | 774 | 1521 | 828 | 87.3 |
| Factor | 1.24 | 0.935 | 1.84 | | |

No attempt was made to recover Freon 113, Alcohol or Zinc from the sludge.

Technical Report on
Fluorocarbon Research at Hooker Electrochemical Company
August and September 1944

TABLE III

Polymerization and Distillation of the Crude Concentrated Polymer

A. Clave Runs and Concentration

| Clave Runs Made | $P_2O_5$ Used Lbs. | Benzoyl Peroxide Lbs. | $CHCl_3$ Used Lbs. | Crude Conc. Produced Lbs. | % | Foreshot from decomposition Lbs. | % | P-539 not accounted for. Lbs | % |
|---|---|---|---|---|---|---|---|---|---|
| 104 | 200 | 832 | 10,740 | 5,723 | 66.4 | 687 | 8.0 | 2,218 | 25.6 |
| Factor | 0.035 | 0.145 | 1.88 | | | | | | |

B. Crude Concentrate Distillation at D.P.I.

| Batch Code | Still Charge Lbs. | Pay Cut Lbs. | Pay Cut % Charge | Residue Lbs. | Residue % Charge | Volatile Lbs. | Volatile % Charge | Loss Lbs | Loss % Charge |
|---|---|---|---|---|---|---|---|---|---|
| A.B.C. | 2,518 | 1184 | 47.2 | 930 | 37.0 | (1) | - | - | - |
| D.E.F. | 1,974 | 911 | 46.2 | 740 | 37.5 | (1) | - | - | - |
| S. | (350) | (2) | - | 0 | 0 | 242 | - | - | - |
| G.H.I. | 1,231 | 565 | 45.8 | 430 | 34.9 | 46 | - | - | - |
| V. | (475) | 240 | - | 0 | 0 | 229 | - | - | - |
| Total | 5,723 | 2900 | 50.6 | 2100 | 36.7 | 517 | 9.0 | 206 | 3.6 |
| % of P-539 | 66.4 | | 33.6 | | 24.4 | | 6.0 | | 2.4 |

(1) Volatiles redistilled as separate batch "S"
(2) Pay cut redistilled as batch "V" with volatiles from "G? H? I"

Technical Report on
Fluorocarbon Research at Hooker Electrochemical Company
August and September 1944

TABLE IV

FM-33 Treatment and Final Distillation

A. F.M.-33 Treatment

| Material Charged Lbs. | F.M.-33 Used | | Total Lbs. | Treated M. F. L. Lbs. | Foreshot Total Lbs. |
|---|---|---|---|---|---|
| | 1st Stage Lbs. | 2nd Stage Lbs | | | |
| 2900 | 2611 | 345 | 2956 | 2466 | 512* |

* Probably contains some $CCl_4$.

B. Final Distillation at D.P.I.

| Finished M. F. L. Lbs. | M. F. L. Residues Lbs. | Low Boilers Lbs. | Degasser Volatiles Lbs. | Vapor Traps Lbs. |
|---|---|---|---|---|
| 1) 1482 | 9.5 | 1) 380 | 1) 190 | 6) 28 |
| 2) 27 | | | | |
| 3) 42 | 7.0 | 14 | 9 | |
| 4) 30 | 5) 1.0 | 16 | | |
| 1581 | 17.5 | 410 | 199 | 28 |

1) In drums at Hooker 1082 pound. One drum containing 400 pounds shipped to Kellex.
2) Samples taken to Kellex Lab.
3) Seven 1/2 gallon samples sent to Miller, estimated to contain 42 pounds M.F.L., 7 pounds residues, 14 pounds L.B., etc.
4) In a 2 gallon can at Hooker - M.F.L. recovered by reworking foreshots and residues - has not been tested by Kellex.
5) Samples sent to Dr Rosen
6) Highly acidic - discarded.